

REACTIONS OF WOOD DURING EARLY COALIFICATION, A CLUE TO THE STRUCTURE OF VITRINITE

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Introduction

Average structural models of coal have traditionally represented coal as a cross-linked macromolecular assemblage of interconnected fragments whose presence in the structure have been inferred from thermal or chemical degradative studies (1-4). To assemble such structures from a melange of fragments existing within some degradative product serves to homogenize a material which is inherently heterogeneous on a macromolecular scale. The structural representations fail to capture this heterogeneity, induced primarily by the existence of macerals representing macromolecularly distinct and possibly internally homogeneous physical entities derived from pre-existing vegetal matter in coal-forming swamps. More realistic structural models can be produced if the individual macerals are considered as discreet homogeneous domains within the heterogeneous mixture known as coal.

For the past several years we have been assembling structural models for individual macerals, focussing initially on vitrinite derived exclusively from xylem of gymnospermous wood (5-9). Studies of such xylem recovered from samples whose rank increases from peat to bituminous coal have provided a wealth of information concerning the molecular fragments and their reaction pathways as they undergo coalification to higher rank. We have been able to ascertain that lignin is the precursor of the vitrinite (5) and that, as such, we can build a structural model with lignin as a template (6, 8). Comparisons among the coalified xylem samples at various stages of coalification by elemental analysis, solid-state ^{13}C NMR, and flash pyrolysis/gas chromatography/mass spectrometry (7,9) provides clues regarding the fate of the various oxygen-containing functional groups. Thus, working from a structural template and altering the template accordingly, a series of structural models representing vitrinite from gymnospermous xylem can be constructed at various rank levels.

Crucial aspects of this approach are 1) the accuracy of the structural model of lignin and 2) the accuracy with which we can define specific coalification reactions. In this paper, we focus on the effect of early coalification reactions on the three dimensional structure of lignin as a prelude to development of a comprehensive model for vitrinite at later stages of coalification.

Coalification Reactions of Lignin

There is mounting evidence that lignin is not a random heteropolymer but an ordered structure. Faulon and Hatcher (10) have recently suggested that lignin assumes an helical conformation of β -O-4-linked glyceryl methoxyphenolic ethers. Although we have used a random structure as a template in previous studies (6, 8), we have now adopted this helical model, shown in Figure 1, as the template.

As coalification of lignin proceeds, some key reactions will modify the chemistry and three dimensional helical structure. Random, large-scale structural reorientations of lignin will likely destroy delicate physical attributes such as bordered pits and cellular walls. The fact that these

physical characteristics of wood persist to the rank of subbituminous coal suggests that the early coalification reactions are likely to be those which cause minimum distortion of the three dimensional structure.

Perhaps the most readily apparent reaction observed in numerous studies (7, 11-13) is the demethylation of lignin. We expect that this reaction has no significant effect on the helical conformation other than to perhaps facilitate hydrogen bonding interactions between helices, because the methyl group is replaced by a hydrogen. The helix is well preserved by this reaction with virtually no change in the cross-sectional size of the helix.

Another reaction which might be expected to induce minimal distortion of the helical structure is dehydroxylation of the hydroxyl groups on side-chain carbons. It is clear from NMR spectra of coalified wood samples at the rank of subbituminous coal that virtually no significant resonances are observed for hydroxylated aliphatic structures, suggesting complete dehydroxylation. Because the aromaticity does not change during this early coalification, we believe that hydroxyl groups have been reduced to alkyl structures. The sp^3 hybridization does not change as a result of this process and, thus, the helical order is not disrupted.

The most significant coalification reaction noted in previous studies (6,8) which has an impact on the helical conformation of lignin is the hydrolysis of the β -O-4 aryl ethers. Rupture of this bond, the primary bond maintaining the structural integrity of the helix, would essentially dismantle the lignin and reduce it to small molecules. If this hydrolysis is the sole reaction, then the lignin would likely be solubilized and removed from the coal. The NMR evidence shows that hydrolysis of the β -O-4 aryl ethers does occur, but a concerted alkylation of an adjacent aromatic ring by the side-chain carbocation formed as the result of hydrolysis maintains the structural integrity of the lignin. The evidence forwarded for such a concerted reaction is manifold. First, evidence for hydrolysis of the β -O-4 aryl ether, though weak, is a decrease in the peak intensity of aryl-O ether carbons in NMR spectra (7). Evidence for increased substitution is provided by dipolar dephasing data which shows a decrease in the average number of protons per ring during the transformation of lignin to brown coal (6). Artificial coalification by Botto (14) of a lignin labeled at the β site shows alkylation to be a significant part of early coalification. The proposed scheme involves cleavage of the β -O-4 aryl ether followed by alkylation of an adjacent ring by the resulting carbocation (8).

Molecular modeling simulations in three dimensional space shows that such a reaction maintains the helical structure of lignin as well as its macromolecular nature (Figure 2). The helix formed by linkages between the β site and the adjacent aromatic ring is of a larger radius and pitch. We would expect that the increased radius of the helix might be expressed at the macroscopic level. Thus, as lignin helices which collectively comprise the cell walls of the peatified wood samples are transformed to helices with larger radii, the cell walls would be expected to show a corresponding size change. Because the axes of the helices are thought to align parallel to the cell walls, any increase in radius will induce cell-wall thickening. Thickening of the cell wall is commonly observed during coalification (15). Photomicrographs depicting the cross-sectional views of peatified wood, composed of essentially pure lignin, and coal wood of subbituminous rank, composed of coalified lignin having undergone cleavage of β -O-4 ethers, alkylation of aromatic rings, and side-chain dehydroxylations, are shown in Figure 3. It is clear that the cell walls are thicker in the brown coal wood, compared with peatified wood. Thus, the model of low-rank coal as a modified helical lignin structure can explain both the observed chemistry and physical morphology.

Conclusions

The modeling of lignin as a helical structure has important implications regarding the structure of vitrinite in coal. If one uses this lignin as a template for coalification, then chemical

changes induced by coalification reactions are likely to affect the helical order. The changes observed in previous investigations do modify the helical structure but fail to entirely disrupt it. These changes are primarily demethylation, side-chain dehydroxylation, and cleavage of the β -O-4 ethers in concert with alkylation of aromatic rings. The three-dimensional changes in the helical order brought about by these reactions are consistent with observed morphological changes in the coalified wood.

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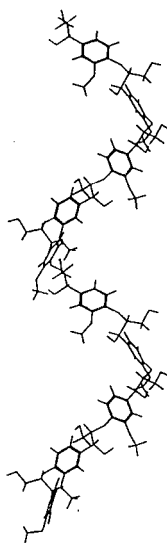


Figure 1. Three dimensional helical conformation for the structure of lignin. This structure has been obtained after energy minimization. The structure is composed of the main monomer (guaiacyl) and linkage type (β -O-4) occurring in lignin.

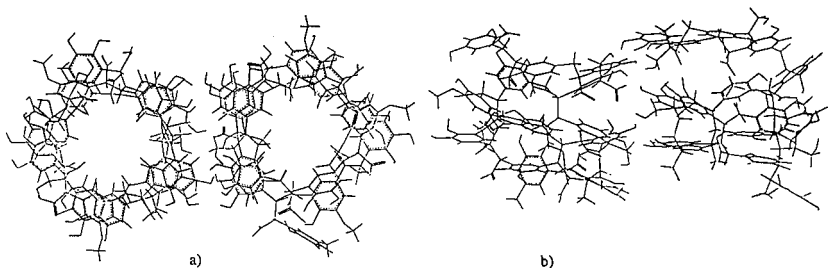
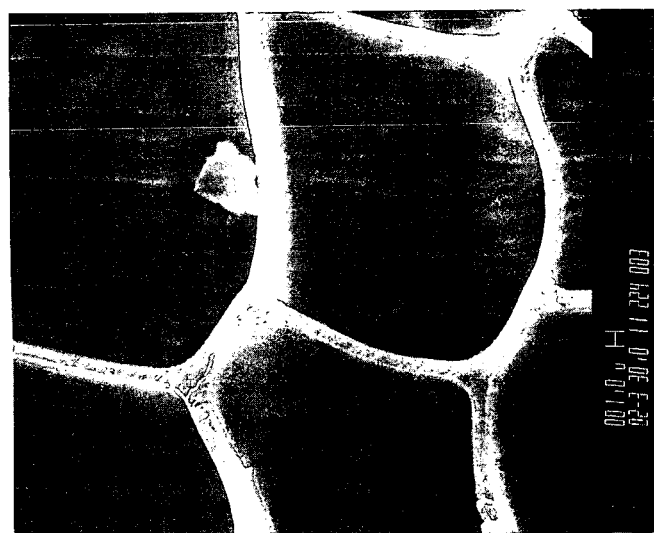


Figure 2. Three dimensional conformation for a lignite rank coalified wood. This lignite structure was obtained by using two helical lignin structures as a template. The initial lignin structures were modified as describe in the text, then, the resulting structure was submitted to molecular mechanics and dynamics simulations to obtained the lowest energy conformation. a) Three-dimensional representation of the structure in plan view. b) Three-dimensional representation of the structure viewed from the side.



a)



b)

Figure 3. SEM photographs of a) degraded wood, and b) subbituminous coalified wood. The two photographs have been taken with the same resolution (the scale indicated at the bottom of the photographs is 1 μm).